Considerations on Super-Heating of Molten Cast Iron

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Considerations on Super-Heating of Molten Cast Iron*

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Synopsis

The elimination of dissolved oxygen by carbon in cast iron melt is of importance in super-heating of cast iron. The decrease of carbon and the increase of silicon content by super-heating are not important in understanding the super-heated melting.

The super-heated fine graphite structure is caused by super-cooling of melt, accompanied by deoxidation, not by solution of graphite nucleus.

I. Introduction

Though super-heated melting of cast iron was tried as early as 1917 by G. K. Elliot(1), it was not till 1925 when E. Piwowarsky(2) made a study on the relation between the melting temperature and the change of combined carbon and on the fining of graphite that scientific attention was widely paid to this phenomenon. Since then these phenomena have been studied by a number of workers. The most conspicuous characteristic exhibited by super-heated molten cast iron is the fining of graphite. This phenomenon has been explained chiefly on the ground that the graphite nuclei in the melt will disappear due to super-heating has chiefly been offered(3), but various other views have also been presented; the nature of this phenomenon remains still obscure. In other words, regarding super-heated melting there are different theories.

Recently in the Europe and America a tendency is prevailing to follow the method of super-heating when cast iron is to be melted. The phenomenon connected with super-heated melting has also an inseparable relation with that of heredity of cast iron. The authors have been studying the heredity phenomemon and succeded in getting a systematic view(4) about it. As a matter of course, the phenomenon of super-heated melting has been examined in the course of the above study and a view concerning this phenomenon is also formed, which will be given below.

II. Theoretical consideration on super-heated melting

1. Change in deoxidizing force of carbon with temperature

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* The 963rd report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of Japan Institute of Metals, **17** (1953), 371.

(1) G. K. Elliot, Foundry, **49** (1921), 714.

(2) F. Piwowarsky, Stahl u. Eisen, **45** (1925), 1455.

(3) H. Jungbluth, Giesserei, **15** (1928), 457; 486.

(4) M. Homma, J. Japan Inst. Metals, **16** (1952), 486; 547; 607; 666.

The change in the deoxidizing force of carbon with temperature is the reverse of what is shown by deoxidizing metallic elements such as Si, Mn, and others, that is, in the case of carbon the deoxidizing force increases as temperature rises, while in the metallic elements it decreases. This has already been treated also in the field of thermodynamics, and the thermodynamical values of deoxidation recently published by Richardson⁽⁵⁾ explain this relation clearly (Fig.1).

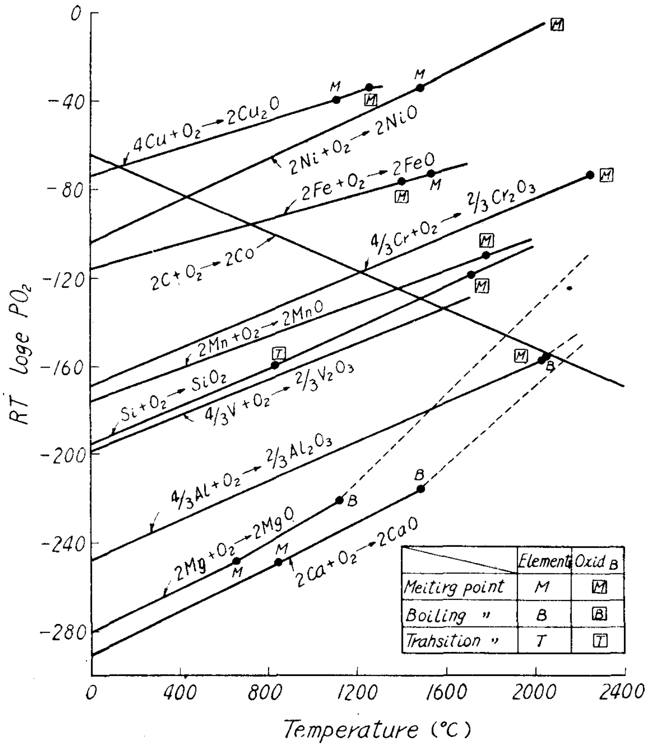

Fig. 1. Thermodynamical values of deoxidation (Richardson).

In this figure all the curves except that of $C+O \rightleftarrows CO$ go upward with rising temperature. The curve with C is the only one that goes downward, because C, contrary to other metallic elements, increases its affinity for oxygen as temperature rises.

The next important thing is that, though it is shown that the curves lower than the curve $Fe+O \rightleftarrows FeO$ have the force to eliminate oxygen from FeO at each temperature, when the two curves $C+O \rightleftarrows CO$ and $Si+O_2 \rightleftarrows SiO_2$ are taken, they cross each other at about 1450~1500°C, which means that Si is more powerful below 1500°C and C is above that temperature. Though this cannot be used directly in comparing the deoxidizing force of each element in steel melt or cast iron melt because it is the equilibrium of each simple oxide, it shows clearly how an element exibits its tendency with temperature change.

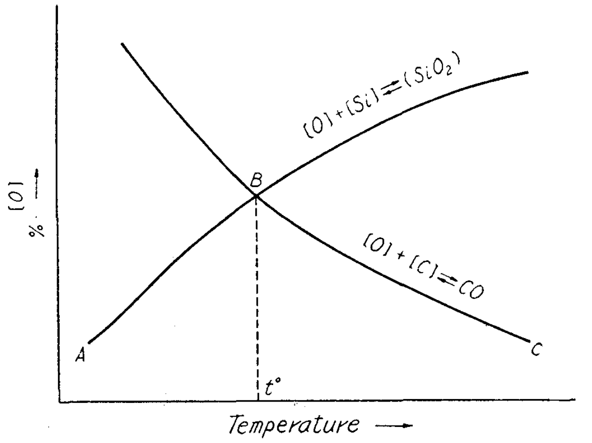

Fig. 2. Relation between temperature and [C]-[O], [Si]-[O].

In Fig. 2 is shown the qualitative relation between the melting temperature and [O] at the fixed values of [C] and [Si] which are obtained from the thermodynamical values of $[O]+[C] \rightleftarrows CO$ and

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(5) F. Richardson, J. Iron and Steel Inst., **160** (1948), 261.

$[O]+[Si] \rightleftarrows (SiO_2)$. As these curves are obtained on the basis of the measured values in dilute carbon solution such as steel, they are only qualitative curves and cannot be applied to such concentrated solution as cast iron melt. But the two curves cross each other at 1450~1500°C, at which the deoxidizing forces of $[Si]$ and $[C]$ exchange the place. The curve ABC forms a deoxidation curve which determines the amount of oxygen contained in melt. Near this turning point of temperature the amount of $[O]$ in melt reaches its culmination and lessens at both higher and lower melting temperatures. In other words, super-heated melting means the melting at temperature higher than the turning temperature at which deoxidation is carried on exclusively by carbon, and gaining deoxidizing force as temperature goes up. Further, the turning temperature is theoretically qualitative, but it is certain that experimentally it comes near to the above-mentioned temperature. The curves of $[C]+[O] \rightleftarrows CO$ in molten steel reported by Marineck, rise gradually with rising temperature on less inclination than that of $[Si]+[O] \leftrightarrows SiO_2$. But as will be shown in our next paper, in the case of the super-heated melting in non-oxidizing atmosphere, it is certain experimentally that the curves of $[C]+[O] \rightleftarrows CO$ in cast iron melt go downward with temperature.

According to the study⁽⁶⁾ at the melting temperature of 1350°C, only Si is consumed by the oxygen which comes from outside, C remaining unchanged in the case of the gradual increase of oxygen in molten cast iron. Further, R. W. Heine⁽⁷⁾ reported on the oxidation of molten cast iron by air that Si was only oxidized at 1300°C and carbon only at 1550°C. But this shows only that in the experiment on oxidation, the combining force of each C and Si with oxygen is stronger at higher and lower temperature than at the turning temperature, and it is chiefly because C forms CO with oxygen which comes from outside and escapes from the melt that C decreased at 1500°C in R. W. Heine's experiment, the carbon contained in the melt decreases and the silicon increases in super-heated melting as will be shown in the next paper. However, the decrease of carbon in super-heated melting is due to the fact that the carbon eliminates the oxygen dissolved in melt by forming a compound CO — a phenomenon of deoxidizing by carbon in melt. One cannot realize the essential significance of super-heated melting so long as one considers that the decrease of carbon in super-heated melting is due to the carbon escaping together with the oxygen of the atmospheric gas, forming the compound CO. The phenomenon of increasing silicon is caused by the reduction by carbon of silicate floating in the melt and SiO_2 in the refractory, and there is no relation between the increase of Si and the formation of super-heated structure.

These are of great importance to one who wants to know the essential significance of super-heated melting.

Fine graphite structure by super-heating has nothing to do with Si content in

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(6) M. Homma, J. Japan Inst. Metals, **16** (1952), 260; 265.

(7) R. W. Heine, A. F. S. Annual Meeting Preprint (1951), No. 51.

cast iron, but it is because the deoxidation is intensified with rising temperature that the melt is super-cooled to make the graphite fine. Now, needless to say that in super-heated melting it is desirable that there be a basic lining to the furnace so that too much SiO may not be reduced from its wall.

2. Breakup of Fe–O–C–Fe cluster by heat

As the activity of some oxygen atoms dissolved in cast iron is weakened by C atoms, it may conveniently be treated as Fe–O–C–Fe cluster⁽⁸⁾ (there are also Fe–O–Si(Mn)–Fe, etc.). Of course, it does not mean that there exists a cluster consisting of fixed Fe, O and C atoms such as molecules, but each of them always changes place with the other which comes next and changes the distance. However, if a momentary meta-crystal structure of melt is taken into consideration, the treatment as a cluster may be possible. And among various types of oxygen in molten metal, the O atoms in a cluster are the ones that serve directly in determining various qualities of iron cast. As the temperature of melt rises, the oscillation between the neighboring atoms in the cluster grains increases, while the combining force between C and O atom grows stronger and stronger until the cluster is difficult to exist. O atom is removed by C and the oxygen content of cast iron melt begins to decrease. This is the significance of super-heated melting in the treatment of oxygen in cluster.

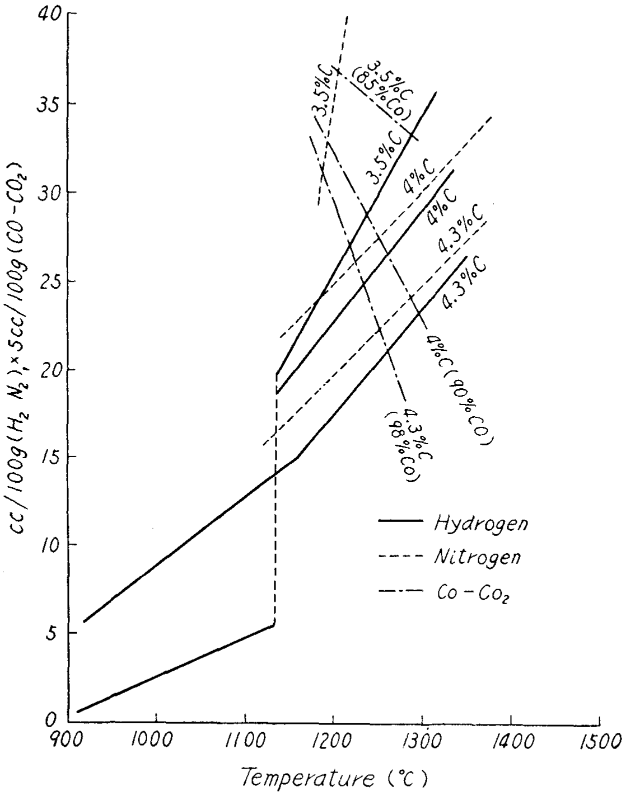

Fig. 3. Relation between temperature and gas solubiliiy of cast iron (Iwase).

3. Absorption of gases by cast iron melt

It is generally known that as temperature rises above the melting point (apart from the boiling point or thereabout), molten metals generally strengthen their absorbing function of other gaseous atoms because the distance between atoms becomes large. As shown in Fig. 3, in cast iron melt, too, the absorbed amount of N_2 and H_2 increases with the rise of temperature. On the contrary, the absorption of CO decreases⁽⁹⁾. This fact does no more than explain the phenomenon that CO which has been absorbed at a lower temperature, goes out of the melt as temperature rises. It seems that

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(8) M. Homma, J. Japan Inst. Metals, **16** (19ç2), 111; **17** (6953), 20.

(9) K. Iwase, Science Rep. Tohoku Univ., **15** (1926), 531.

A. Schneble and J. Chipman⁽¹⁰⁾ also exclude the accepted graphite-nucleus theory with respect to super-heated melting and find its cause in the presence of gases, especially CO, in melt.

The three phenomena mentioned above are the same thing considered from three points of view—the purpose of super-heated melting is to deoxidize, especially to remove the O atoms which serve directly in determining the qualities of cast iron. The characteristic of deoxidation by carbon in super-heating is that the carbon and oxygen which have already been in the melt gain their closer affinity with rising temperature and escape from the melt as CO, while in other cases of deoxidation by such metallic elements as Si and Mn, those elements are thrown into the melt from outside to remove the oxygen present in it. Needless to say that to attain the purpose of super-heated melting the atmosphere with oxidizing condition is undesirable.

III. On the nuclear theory explaining the shape of graphite

Attempts have been made to explain the shape of graphite of cast iron by insoluble nucleus present in the melt. The opinion, for instance, held by von Keil⁽¹¹⁾ that ferrous silicate slime is the cause of flake graphite or the view that nucleus of Si–Mg or other Mg compound produces nodular graphite belongs to this group. But they are considered to be mistaken. All that can be said is that the presence of nucleus makes it possible to crystallize with less energy of crystallization, compared with the case where there is no such nucleus. Even if there is no such nucleus, it can crystallize by generating its own crystallizing nucleus if it obtains work energy necessary for crystallization. Moreover, it is generally unreasonable to think that the existing nucleus or its shape influences the shape of a crystal to be formed. Becker⁽¹²⁾ gives Fig. 4 to clarify the relation between work function $F_{(a)}$ for producing a crystallizing nucleus and the diameter of the nucleus a. Before a nucleus with diameter a_0 is produced and so long as the energy for producing a crystallizing nucleus does not grow to A, the crystallizing nucleus remains unstable, appearing and disappearing as the energy becomes strong or weak, but once it has grown to the critical size of diameter a_0, it no longer needs much energy and grows. It is a matter ot course that if there is some non-metallic inclusion or insoluble graphite in the diameter larger than critical size a_0 (even though smaller that if ever insoluble nucleus), graphite can crystallize itsely from melt more easily with them as

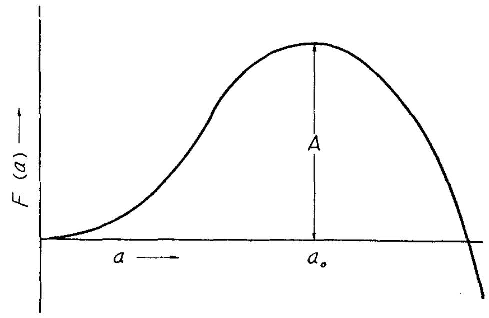

Fig. 4. Relation between work function for producing nucleus and nuclear diameter (Becker).

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(10) A. Schneble and J. Chipman, Trans. Amer. Found. Asoc., **52** (1944), 113.
(11) von Keil, Arch. Eisen., **4** (1940), 245.
(12) R. Becker, Z. Metallkunde, **29** (1937), 245.

crystallizing nucleus than it can where there are no such things. And even though there are no such things at all, the graphite crystal, after it has once reached a_0 with the supply of energy for producing crystal, never vanishes, but grows without any further supply of such energy. And when graphite is crystallized, its crystallized shape is not at all affected by the influence of the existing nucleus, but changes according to the influences of its own properties and outward conditions which have effect on the crystallized shape, that is, the qualities of melt. As has been reported(4), at normal melting temperature (1300~1450°C) the structure changes according to the change in the amount of oxygen dissolved in melt, that is, by increase of oxygen, flake graphite (I) gradually tends to rose graphite (II), eutectic graphite (III), inverse chill structure (IV), and white cast iron structure (V), and by decrease of oxygen, flake graphite (I) gradually tends to rose graphite (II′), eutectic graphite (III′), fine graphite (IV′), inverse chill structure (V′), and super-cooled white cast iron structure (VI′). If fine structures of graphite (structures III and III′~IV′) are formed by graphite nucleus not existing, according to the old nucleus theory, it follows that graphite nucleus exists only when the oxygen amount in melt is intermediate (II~I~II′), and does not exist when that is either more (III) or less (III′). This cannot convince us. It can be thought that fine graphite in cast iron is due to super-cooling caused by deoxidation of melt (III′~IV′), to increased action by oxygen of preventing the growth of graphite (III), or to super-cooling brought about by rapid cooling, but not to the non-existence of graphite nucleus in melt. In super-heated melting, the deoxidation of melt by carbon results in forming III′~IV′ structures.

The opinion held by von Keil that floating silicate nucleus is the direct cause of flake graphite is not adequate, for it is naturally thought that floating silicate increases according as the oxygen in melt increases. On the other hand, in the structural change described above, the shape of graphite becomes smaller and smaller, from flake graphite structure (I) to rose graphite (II) then to eutectic graphite (III) oxygen increases. This shows that eutectic graphite (III) is also formed by silicate nucleus. In regard to the formation of nodular graphite two contrary opinions exist: one is that nodular graphite is caused by the existence of some crystallizing nucleus other than graphite, and the other is that this is not the case. It is true that where there is some other kind of nucleus in melt, nodular graphite tends to come into being earlier than in other places, but the existence of some nucleus beforehand is not the indispensable condition for nodular graphite to crystallize itself. Neither is it thought that there is direct relation between the shape of crystallized graphite being nodular one and existing insoluble nucleus. The authors think that an extremely small amount of dissolved oxygen is one of the most convenient conditions under which graphite is made nodular. As has been stated, hypo-eutectic iron melt with an extremely small amount of oxygen is solidified into nodular graphite cast iron or into white cast iron (VI′), which then precipitates nodular temper graphite after solidification, if the cooling speed is slow and the Si amount is large. From hyper-eutectic iron melt with an extremely small amount of oxygen, kish graphite which is crystallized in the melt takes nodular shape.

Summary

(1) The essential significance of super-heated melting is the elimination of dissolved oxygen in cast iron melt by carbon. This considered in this paper from the theoretical standpoint. The decrease of carbon in melt, if ever, as a result of forming CO with the oxygen in the atmosphere has no bearing on the essential significance of super-heated melting.

(2) In super-heated melting silicon in melt tends to increase in amount, but this is not of essential significance. For instance, super-heated fine graphite structure has no relation to the amount of silicon.

(3) The explanation of fine graphite formation by solution of graphite nucleus in cast iron melt is not convincing. It is considered a mistake to try to explain the shape of graphite by the existence of insoluble nucleus such as von Keil's ferrous silicate theory, or the theory of Mg compound nucleus.